

The X-ray *L*-absorption spectrum of silver

A study with bent crystal and proportional counter

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With 17 figures in the text

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ABSTRACT

A bent crystal-vacuum spectrometer is described as well as the detector system employing a proportional counter. The three *L*-absorption edges of silver are recorded in such a way that the *absolute* value of the mass absorption coefficient is determined as a function of wavelength, and curves of these functions are published. Special attention is paid to the fine structure in the absorption spectra within a region of around 60 eV on the high energy side of the absorption limit. The influence of the resolving power of the spectrometer on the recorded spectra is discussed. The wavelengths and energies of the absorption limits are measured, with the following results: L_{III} : $\lambda = 3692.1$ XU, $E = 3351.0$ eV; L_{II} : $\lambda = 3509.3$ XU, $E = 3525.5$ eV; L_I : $\lambda = 3249.8$ XU, $E = 3807.0$ eV.

Introduction

The present investigation is the first in a series intended to cover the *L*-absorption spectra of the elements in the region 47 Ag–52 Te. As the apparatus and method will be identical for the whole region these are described in detail only in the present paper, and a summary and discussion of the final results will be given in a special paper to be published later. The disposition of the material in the present paper, where the experimental results are given relatively little space, must be seen in the light of this.

In 1926, Coster & Mulder [1] measured the *L*-absorption limits for silver. The registration was photographic, and as absorber the AgBr emulsion in the plate was used. Thus their results do not refer to pure Ag metal. Van Dyke & Lindsay [2] repeated the measurements a year later, using a rolled Ag foil as absorber. The registration was still photographic, however, and the absorption spectrum was definitely greatly disturbed by the absorption in the photographic emulsion. In neither case were any photometric curves published. In 1938, Parratt [3] published a paper on Ag *L*-spectra recorded with an ionization chamber. The three *L*-absorption edges form part of this investigation, though only that of L_{III} is published. Parratt gives no wavelength or energy value for this absorption limit, but from the published curve with its wavelength axis one can compute an approximate value.

The present investigation is thus the first published study of the structure of the L_I and L_{II} edges of metallic silver at the same time as it results in the first non-photographic wavelength and energy determinations of the three *L*-absorption limits.

I. The spectrometer

The present investigation was carried out with a vacuum spectrometer of the Johann type, designed by Sandström. In two papers [4, 5] he has given a detailed description of its construction and adjustment as well as a discussion of its resolving power. A short account may also be found in Encyclopedia of Physics [7], pp. 114–116. Since the papers were published changes have been made concerning the X-ray tube, crystal mounting, slit, absorption foil holder, pumping system and detector system. The new X-ray tube, which is a twin tube with two targets and two oxide cathodes, has previously been reported [6]. Before describing the other changes, however, the principle of the spectrometer will be briefly stated for the sake of completeness.

1. The principle of the spectrometer

Fig. 1 shows schematically the construction of the spectrometer. *CS* is a direction fixed horizontally in space, and *CP* and *SP* levers joined at *P* by an elbow joint. Their length is $R/2$, where R is the curvature radius of the crystal. The crystal surface is perpendicular to the lever *CP*. At the upper end of the lever *SP* (the point *S* in the figure) a slit is placed, and this point together with the slit can be moved along the direction *CS* by means of a precision screw, keeping the point *C* fixed in space. Thus *CS* is always a chord in the focussing circle, and X-rays from the target *T* on the circle will automatically be focussed on the slit for any position of the latter. In the present case a linear X-ray target focus is used, placed close to the crystal on the line *CT*. The angle of incidence for the radiation is not set automatically but determined in a way described later.

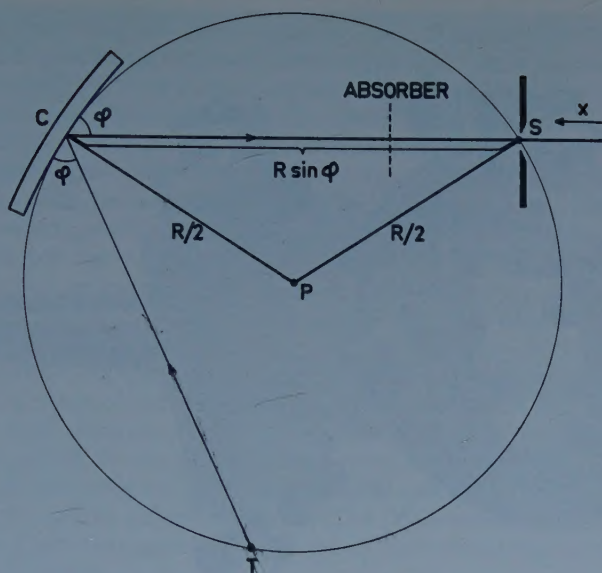


Fig. 1. The principle of the spectrometer. T is the X-ray source, C the crystal and S the slit.

With this arrangement the dispersion of the spectrometer, $\Delta\lambda/\Delta x$, where x is the distance along the precision screw, will be independent of φ :

$$\Delta x = -\Delta(R \sin \varphi) = R \cos \varphi \Delta \varphi;$$

and from Bragg's law:

$$n \cdot \Delta \lambda = 2 d_n \cos \varphi \Delta \varphi,$$

which gives

$$\frac{\Delta \lambda}{\Delta x} = -\frac{2 d_n}{n R}. \quad (1)$$

As the spectrometer is used for relative wavelength measurements only, a constant dispersion is naturally of great value.

The angular region of the spectrometer is 33° – 80° , where the lower limit is set by the angle at which the elbow joint P reaches the bottom of the vacuum tank. The upper limit is determined by the screening of the reflected X-rays by the X-ray tube.

The crystal used in the present investigation is quartz 1010, which gives the following wavelength regions:

1st order	4600 XU–8360 XU
2nd order	2300 XU–4180 XU
3rd order	1530 XU–2790 XU
4th order	1150 XU–2090 XU.

Reflexions in orders higher than the 4th are extremely weak.

The crystal curvature radius was determined experimentally by placing four

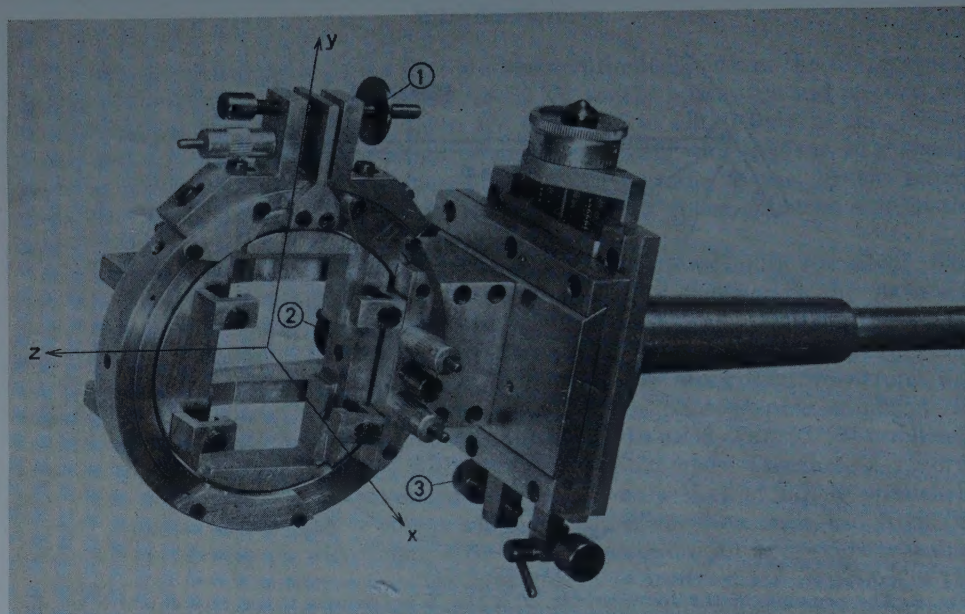


Fig. 2. The crystal block holder. The adjustment screws 1, 2 and 3 rotate the crystal round the x , y and z axes respectively. The bending block fits into the rectangular opening and is fastened by the four clamps.

photographic plates at different points along the direction CS and exposing each in turn to $\text{Cu } K\alpha_1$ radiation. The half-widths of the lines were measured on their photometric curves, and the position for the best focussing determined by interpolation. The radius was found to be (2006 ± 2) mm, and the lengths of the levers CP and SP were adjusted accordingly [4]. Eq. 1 then gives for the dispersion of the spectrometer, using the lattice constant values listed in ref. [7]:

1st order	4.232 XU/mm
2nd order	2.117 XU/mm
3rd order	1.411 XU/mm
4th order	1.058 XU/mm

with an accuracy of 0.1 %. The dispersion has been experimentally measured in the 2nd order, using 13 pairs of reference lines distributed over a great angular region. The weighted mean of these determinations is 2.116 ± 0.003 XU/mm (mean error). The close agreement with the calculated value indicates that one reference line is sufficient in cases where the distance between this and the "unknown" structure is not too great. As good reference lines are scarce, this property of the spectrometer is most valuable.

2. The crystal mounting

The crystal-bending block is described in ref. [4], p. 527. This block is mounted in a block-holder (Fig. 2), which for adjustment purposes permits a rotation of the

crystal around three mutually perpendicular axes. This is done by means of three screws 1, 2 and 3, producing rotations around x , y and z axes respectively. The generatrices of the crystal cylinder surface are parallel to the z axis. The adjustment of the z -rotation as well as adjustments of the cross-table were made permanently as described in ref. [4]. The description of the basic adjustment of the x - and y -rotation is also given there. The screws 1 and 2 have spring-loaded counter pins, and these adjustments can thus be made from outside the spectrometer, using flexible axles, which makes controls and improvements possible while the spectrometer is working. As the criterion for the best possible adjustment is a maximum resolving power, the half-width of an emission line is a suitable control measure. The following method was therefore employed. The spectrometer was set for a narrow line with a Bragg angle close to one end of the angular region ($\text{Fe } K\alpha_1$; 4th order). This line was recorded for a number of different settings of screw 1, the x -rotation between each setting being 3 minutes of arc. The setting giving the smallest half-width was chosen. The same was then done for screw 2 with y -rotation in steps of $8'$. Finally, the x -rotation was repeated, giving a new setting very close ($< 6'$) to the first one. Then the spectrograph was reset for a line at the other end of the angular region ($\text{Fe } K\alpha_1$; 3rd order) and the whole process repeated. The difference in optimum screw setting for the two cases was very small and a mean value could safely be chosen, giving the best overall adjustment.

3. The slit

When changing the width of the original slit the whole slit-frame had to be removed, a rather cumbersome operation. A new and more convenient type was therefore constructed, where the width could easily be varied between 0–0.15 mm by means of a screw. As only one of the slit-halves is movable, the position of the centre of the slit will vary with its width. This variation is too small to be of any significance to the adjustment of the spectrometer, but a consequence is that reference lines must always be recorded with the same slit-width as the structures whose wavelengths are to be measured.

Given a fixed geometrical slit-width the wavelength region admitted by the slit will vary with the setting of the spectrometer. Let the geometrical width be $2a$. Its angular width $\Delta\varphi$ (see Fig. 1) is then

$$\Delta\varphi = \frac{2a}{R \sin \varphi}. \quad (2)$$

From Bragg's law follows

$$n \Delta\lambda = 2 d_n \cos \varphi \Delta\psi,$$

and the wavelength region $\Delta\lambda$ admitted by the slit is thus

$$\Delta\lambda = 2a \frac{2d_n}{nR} \cot \varphi = 2a D_n \cot \varphi, \quad (3)$$

where D_n is the n th order dispersion.

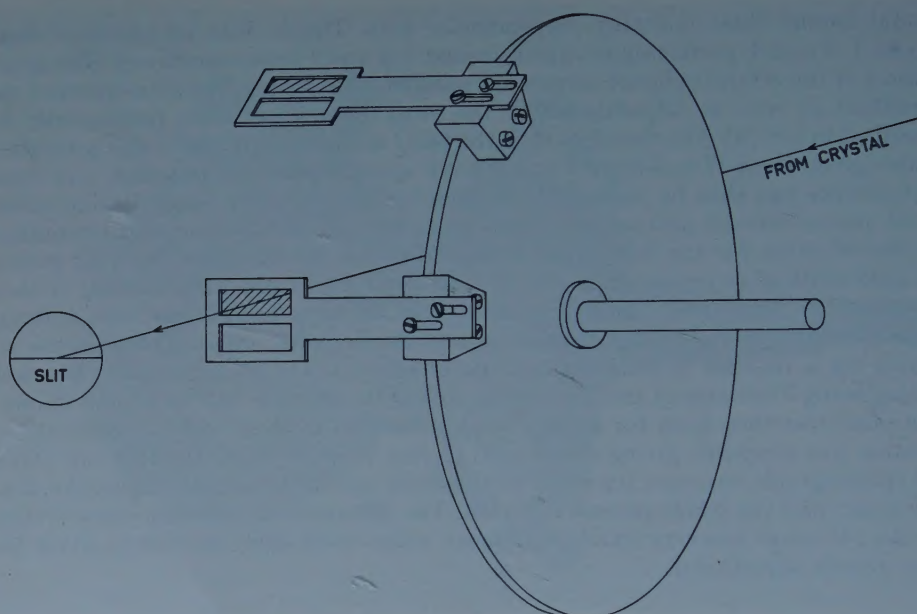


Fig. 3. The absorber frames and their mounting on a disk that can be rotated from outside the spectrometer tank. The direction of the X-radiation is indicated.

During the present investigation the slit-width has for intensity reasons been chosen at maximum opening 0.15 mm. In Section VI, where the influence of the slit-width on the resolving power is discussed, it will be shown that this great width does not seriously affect the resolution.

4. The absorption foil holder

The absorbers are mounted on aluminium double frames with two identical windows 8×25 mm (Fig. 3). Both windows are covered with the substrate (mylar) while one of them in addition has a layer of the metal to be investigated. The frames are clamped to an aluminium disk (Fig. 3), which can be turned from outside the spectrometer by means of a gear system and a vacuum-tight manipulator. The assembly is fastened to the spectrometer base between crystal and slit at a spot indicated in Fig. 1. Immediately in front of the disk an aluminium screen is placed with a rectangular aperture slightly larger than one of the absorber windows. The centre of the aperture is on the line connecting the centre of the crystal with the centre of the slit. The screen serves the purpose of fixing the position of the absorber frames as well as decreasing background radiation.

5. The pumping system

The vacuum volume of the spectrometer tank is around 2000 l and a high pumping speed is thus desirable. The old pumping system dating from 1948 did not fulfil the demands of today in this respect and was replaced by a system consisting of an

Edwards backing pump S150 plus an oil diffusion pump F603, also from Edwards. The pumping speed of the latter is 650 l/sec on the unbaffled pump, and it is connected to the spectrometer tank with as short and wide tubes as possible. Immediately above the diffusion pump is a liquid-nitrogen trap. The vacuum-meter tubes (Pirani and ionization gauge) were removed from their original position close to the pumps to the opposite end of the spectrometer tank. A pressure of $1-2 \times 10^{-6}$ mm Hg, as measured with the Standard Radio 3531 B ionization gauge, can be kept during recordings. It takes about 5 hours to reach this vacuum from full atmospheric pressure. One condition for a good vacuum is that water vapour is avoided as much as possible. For this reason a glass tray with P_2O_5 is always kept inside the tank, and when it is necessary to open the latter the air is admitted via a drying tube containing silica gel.

II. The detector system

The spectrometer was originally equipped with a GM counter, placed immediately behind the slit [5]. For emission studies this arrangement was satisfactory, but when the absorption investigations started it was soon found that there were serious drawbacks. All measurements were limited to the 1st order spectrum and the X-ray tube tension had to be kept below twice the excitation voltage for the radiation in question. Furthermore the efficiency of the counter was unsatisfactory as the counter gas pressure had to be kept fairly low (around 100 mm Hg) in order to avoid excessive counter voltages. Finally, the background counting rate was rather high.

Brief experiments were made with an electron multiplier with copper-beryllium dynodes according to Allen [8], but its efficiency was found to be very low in the energy region considered (2-5 keV). A photomultiplier would hardly be suitable since the noise would be of the same order of magnitude as the pulses from the X-radiation.

The detector best suited for the present purpose is the proportional counter, which in combination with a channel discriminator effectively eliminates or reduces all the drawbacks mentioned above. Absorption spectra can be recorded in any order reflected by the crystal, and a high X-ray tube voltage can be used making high emission currents possible and thus greatly increasing the radiation intensity. As the proportional region lies at lower counter voltages than the GM region the gas pressure can be chosen fairly high (atmospheric pressure or more) without reaching uncomfortably high counter voltages. Finally, the background counting rate will be low owing to the channel discriminator.

1. The proportional counter

The proportional counter (Figs. 4, 5 and 6) is of a cylindrical type with a length of 20 cm and a diameter of 2 cm. It is made of a square brass rod, bored to the dimensions above. It has two side windows placed diametrically opposite each other: an entrance window 2×15 mm and an exit window 3×20 mm. The latter decreases the risk of spurious counts due to photo-electrons ejected from the counter-wall by the incident X-radiation. Both windows are covered with mylar films of a mass thickness of 0.9 mg/cm^2 . They are fastened to the counter-body with a frame of sticky tape, which is pressed against the counter by a rubber frame and a covering plate. In this way practically completely gas-tight windows are obtained, standing

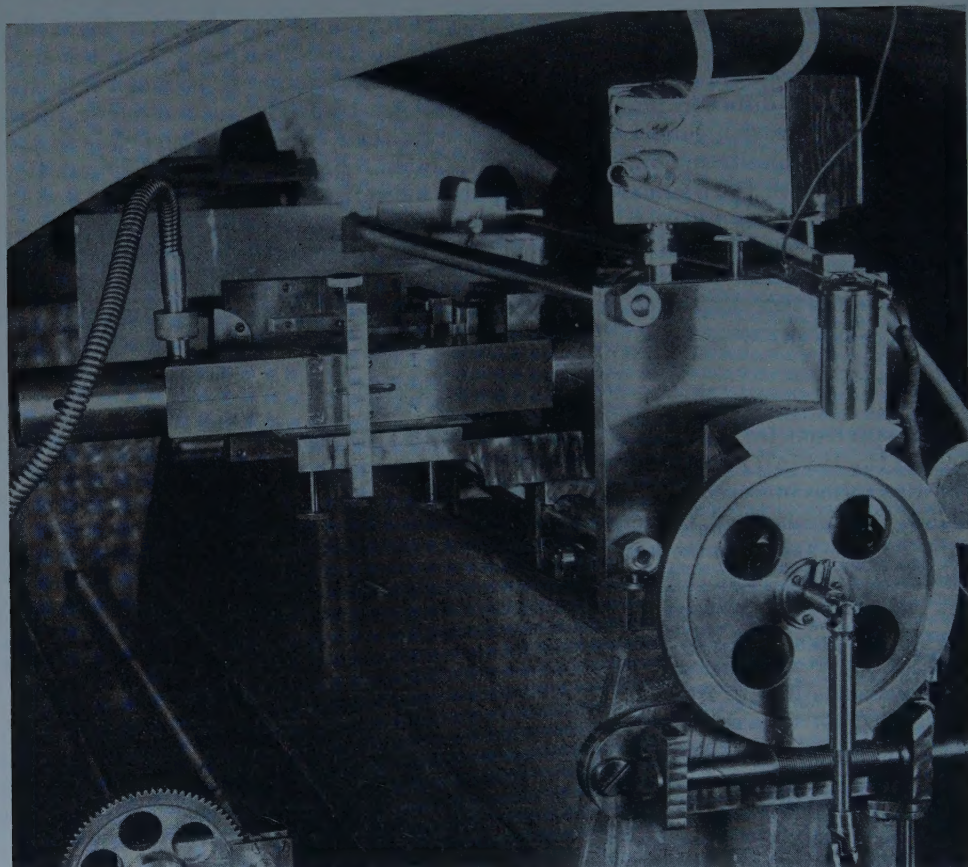


Fig. 4. The proportional counter *in situ* inside the spectrometer tank. The exit window of the counter is turned towards the reader. The box in the upper right corner of the picture contains the cathode follower.

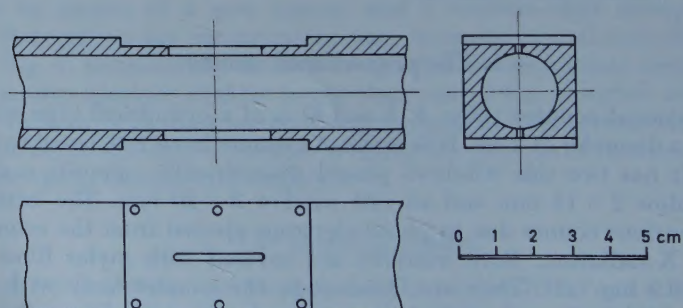


Fig. 5. The central part of the proportional counter body.

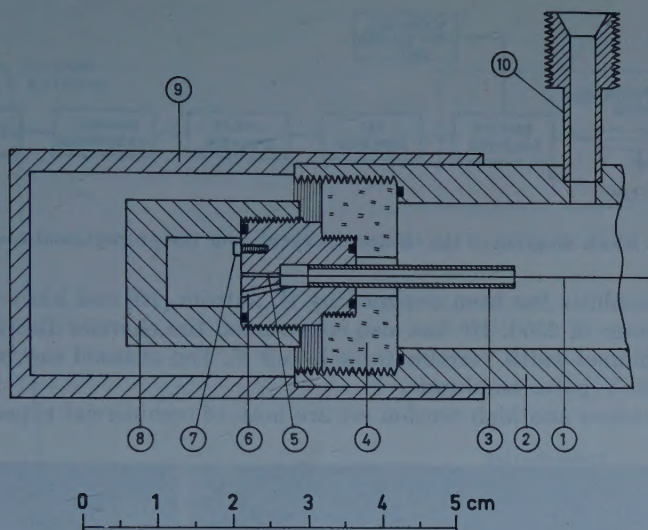


Fig. 6. The construction of the counter ends. 2 is the counter body. The central wire 1 is pulled through a narrow hole 5 and fastened under the head of screw 7. 3 is a tube at wire potential to prevent avalanches from forming close to the counter ends. 4 is a plexiglass insulator. The cap 8 makes the counter end vacuum tight, and 6 is an evacuation channel for the volume under the cap. The end is electrically screened by a cylinder 9. The cylinder at the other end of the counter is equipped with a coaxial connector making electric contact with 8 by means of a spring. 10 is a tube for evacuating and filling the counter. The black rectangles indicate the positions of the "O" rings.

pressures of more than 1000 mm Hg from either side. The transparency of the mylar film is around 90 % at the wavelengths considered here [9].

In order to facilitate dismounting for cleaning, the counter ends are sealed with "O" rings according to Fig. 6.

The central wire is of stainless steel and has a diameter of 0.08 mm. It was supplied by Fagersta Bruks AB, Sweden. Inspection under a microscope revealed a high degree of uniformity, which is important for a good resolving power of the counter.

Before assembling the counter the cathode cylinder is polished with fine abrasive paper and, like the central wire, cleaned with alcohol.

2. The electronics system

The block diagram in Fig. 7 shows the electronics system for the proportional counter, consisting of a cathode follower, a preamplifier, a linear amplifier, a channel discriminator and a stabilized high-tension set. The units are arranged as seen in Fig. 8.

The cathode follower is placed inside the vacuum tank as close as possible to the counter (Fig. 4), to which it is connected with a coaxial cable. Its circuit diagram is found in ref. [10], p. 218. The gain is 0.6.

The preamplifier, consisting of two amplification stages plus a cathode follower, has a fixed gain of 100. It is described by Elmor & Sands [11].

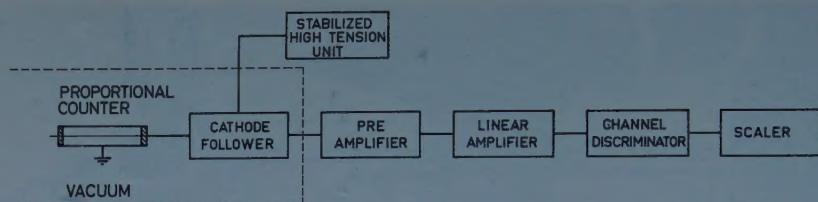


Fig. 7. Block diagram of the electronics system for the proportional counter.

The linear amplifier has been designed by B. Åström [10] and has a variable gain up to a maximum of 2500. He has also constructed the channel discriminator [12], which has a channel-width variable from 1 to 9 V. The channel can be set inside a region of 0–100 V pulse amplitude.

Finally, the scaler and high tension set are both of commercial types. The former

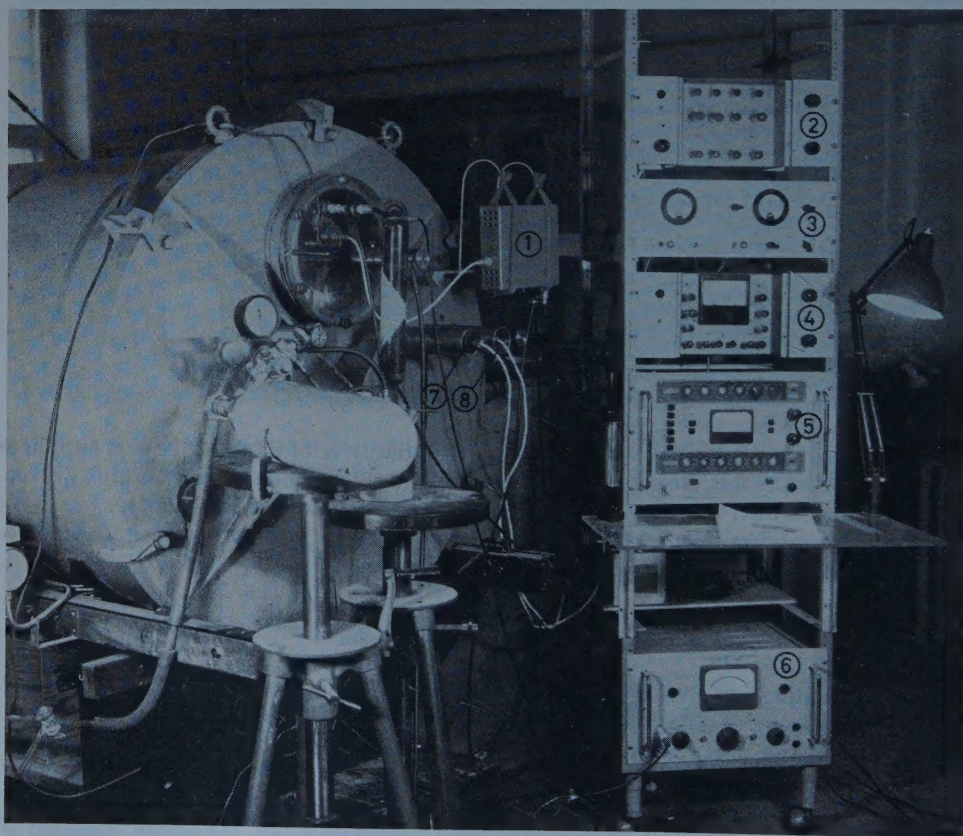


Fig. 8. The arrangement of the electronics units for the proportional counter: 1 preamplifier, 2 linear amplifier, 4 channel discriminator, 5 scaler and 6 high tension unit. 3 is the electronics for the ionization gauge 7 and Pirani gauge 8. The gas tubes in front of the tank gable contain krypton and methane for filling the counter.

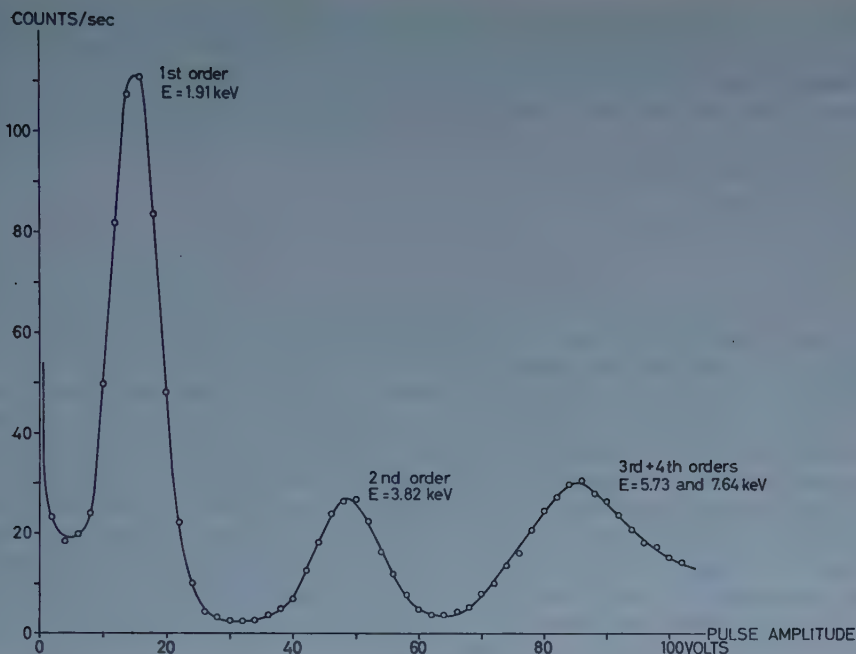


Fig. 9. Pulse spectrum of the radiation entering the counter when the Bragg angle is 50° . The channel width is 4 V.

is from EKCO Electronics Ltd. and has the type number N530F, and the latter, adjustable up to 3 kV, was supplied by Isotope Developments, type 532/D.

With the comparatively high total amplification used (of the order of 10^5), it has proved essential to employ screened cables for all connections. Further, the heater current for the cathode follower and preamplifier is taken from a 6 V lead accumulator placed in a screening metal box. With these precautions no pulses except those from the counter were registered for discriminator settings $> 1 \text{ V}$.

3. Performance of the detector system

(a) Resolving power

When the spectrograph is set at a certain Bragg angle φ , the crystal reflects a series of wavelengths λ_φ/n ($n = 1, 2, \dots$) out of the incident continuous radiation. As already mentioned, the present detector system makes it possible to select one of the orders only. Fig. 9 shows a pulse spectrum of the radiation entering the counter. The channel-width is 4 V. The X-ray tube voltage is high enough (12 kV) to generate four orders of radiation. The wavelength of the lowest is 6480 XU, which corresponds to an energy of 1.91 keV. Owing to the basic property of a proportional counter the pulse peaks should be separated by a constant amount, and this is also the case for the first three. Here, however, the 4th order is unresolved from the 3rd owing to the amplifier being nonlinear for output pulses $> 90 \text{ V}$.

The pulse spectrum in Fig. 9 makes it possible to measure the resolving power

of the detector system, defined as the relative width at half maximum of the peaks. It is in the 1st order (1.91 keV) 27 % and in the 2nd (3.82 keV) 17 %. As a comparison it may be mentioned that Curran in his article on proportional counters in the *Encyclopedia of Physics*, volume XLV [13], has a diagram giving 31 % and 21 % as typical values for these two energies. The resolving power of the present system must thus be considered satisfactory.

(b) *Background radiation*

The curve in Fig. 9 is uncorrected for background radiation. As pointed out in a previous paper [14] in the present case most of the background is secondary radiation from the crystal holder and the crystal itself. The main radiating elements here are aluminium (cover on the crystal bending block), silicon (the quartz crystal), and nickel and iron (the block-holder). A spectral analysis of the background radiation, performed with the X-ray tube turned away from the correct Bragg angle in order to eliminate the coherent radiation and using the channel discriminator as a spectrometer, revealed two peaks at the approximate energies 1.7 keV and 7.4 keV. The first peak closely coincides with the *K* radiation from Al and Si, while the second one evidently is the *K* radiation of Ni and Fe. As the intensities of these peaks are rather high, absorption measurements at energies in the neighbourhood of them cannot be performed with good accuracy. When this is required, however, screens made of other materials can always be arranged in front of the crystal, shifting the background peaks to other energy regions.

(c) *Mixing of orders*

The present measurements were performed in the 2nd order, where the background intensity is low. From Fig. 9 it is clear that this order is well resolved from the 1st and 3rd ones, and with the channel placed on the centre of the pulse peak no serious mixing of orders occurs even if the channel-width is somewhat wider than 4 V. In fact, during the recording of spectra the width was for intensity reasons chosen at 9 V, and an influence from the surrounding peaks was noticeable only when very strong emission lines were present in these. Such lines can, however, be removed when necessary by using another target material in the X-ray tube.

Mixing of orders can also be due to the presence of escape peaks. These are observed when the incident photon ionizes a counter gas atom in an inner shell, and the atom is de-excited by the emission of an X-ray quantum which is not reabsorbed in the gas. The counter then registers an energy which is the difference between that of the primary photon and the binding energy of the ejected electron. However, if the de-excitation is an Auger process or if the secondary photon is absorbed in the gas, the total energy is registered. A concept of importance in this connection is that of the fluorescence yield. This states the probability that an ionized atom is de-excited by X-ray emission and is thus connected with the intensity of the escape peaks.

In the present case the most common proportional counter gas, argon, cannot be used, as the *K*-escape peak, generated by the 4th order radiation, would coincide with the 2nd order. The disturbance is quite considerable owing to a fairly high value, 0.11, of the fluorescence yield. Instead a mixture consisting of 90 % krypton + 10 % methane was chosen, and the counter filled to a pressure of around 800 mm Hg. In the case of krypton the energy of the 4th order radiation (the highest order

present) is insufficient for generating a K -escape peak. The L -escape peak from the 3rd order should coincide with the 2nd order, but no such disturbance could be detected. This is explained by the low L -fluorescence yield, around 0.03 [15], plus the fact that the secondary L -radiation is of a low energy and thus to a great extent reabsorbed in the gas.

To sum up, it may be said that for all practical purposes, the pulses counted with the 9 V channel in the 2nd order position emanate only from the 2nd order radiation, with the exception of background counts. The influence of the latter can be removed by corrections performed according to a method described earlier [14].

(d) *Running conditions*

As mentioned above, the gas pressure in the counter is 800 mm Hg. For X-radiation at 3.5 kXU (Ag L -edges) this gives a linear absorption coefficient of 2.52 cm^{-1} , calculated according to Jönsson's formula [7]. Over the 2 cm path in the counter the transparency of the gas is then less than 1 %, and as the absorption in the counter window is around 10 % [9], the quantum counting efficiency is 90 %.

The total amplification was 6×10^4 , distributed over the cathode follower 0.6, preamplifier 100 and main amplifier 1000. With a tension of 2400 V on the counter anode the amplified pulses from the 2nd order radiation (3.5 keV) have an amplitude of around 50 V, i.e. within the region best suited for the discriminator. The pulse amplitude at the counter anode turns out to be of the order of 1 mV.

An estimation of the gas multiplication of the counter can also be made. The pulse at the wire has an amplitude determined by

$$V = \frac{A n e}{C}, \quad (4)$$

where A is the gas multiplication, n the initial number of ion pairs, C the electrical capacity of the counter electrode system, and e the elementary charge. C is in the present case around 5 pF. The ionization potential for krypton is around 14 V, and as the energy of the radiation is 3500 eV one can expect circa 250 initial ion pairs. The relation (4) then gives $A \approx 125$, a very normal value, indicating that the counter is operating well within the region of proportionality.

The discriminator setting was determined by scanning the 2nd order pulse peak with the 9 V channel and selecting the position giving the maximum counting rate. This was done as a routine adjustment every morning and repeated during the day if judged necessary. On the whole the setting was the same from day to day within the same X-ray energy region, but variations of one or two volts could occur, probably owing to temperature changes in the room affecting the pressure of the counter gas and the performance of the electronic circuits. Over a period of weeks greater variations were found, and these are assumed to originate in a poisoning of the gas by the brass walls of the counter and a very slow gas leakage. For this reason the counter was refilled *in situ* about once a month and taken out for thorough cleaning twice a year. With that kind of service the counter has always been very stable and reliable.

III. The absorption foils

The Ag foils used as absorbers were manufactured by vacuum evaporation, using an evaporation chamber designed by Lennander [16]. The substrate was mylar film

with a mass thickness of 0.86 mg/cm^2 . The carefully cleaned film was stretched over a copper plate and covered by another plate with a window somewhat larger than one of the foil holder windows. The silver metal was placed on a tungsten strip that had previously been cleaned and heated in vacuum. The distance between the boat and the substrate was 14 cm. The silver metal used was of spectroscopically standardized quality, supplied by Johnson, Matthey & Co.

The pressure in the chamber was around $3 \times 10^{-6} \text{ mm Hg}$ immediately before the evaporation but increased to around 10^{-5} mm Hg during the process.

According to a previously published paper [14], there is an optimum absorber thickness determined by the value of the absorption coefficient and the background radiation, which gives a minimum statistical error in the absorption coefficient measurement. Using an Ag foil with a known thickness the parameters necessary for calculating the optimum thickness were obtained as described in the paper cited above. The region of the absorption spectrum where the highest statistical accuracy was desired was judged to be the fine structure on the high energy side immediately before the absorption limit, and for this the optimum thickness should be 1.8 mg/cm^2 . From trial evaporations the amount of silver necessary to obtain this thickness was estimated, and the final absorber was found to be $1.45 \pm 0.07 \text{ mg/cm}^2$ (standard error). The deviation from the optimum value is insignificant, as this is not critical [14].

According to a paper by Parratt [17], an absorber should be as thin as possible in order to minimize the distorting influence of the spectral window on the measured absorption spectrum. For this reason the optimum thickness according to [14] cannot always be chosen. In the present case, however, the optimum thickness is so small that the distortion will not be too great. This will be further discussed in Section VI.

The absorber thickness was measured by weighing on a sensitive balance. This method gives the mean thickness of the foil. That the evaporation method gives foils of macroscopically uniform thickness was tested by cutting a foil into strips and determining the thickness of each strip. However, a certain microscopic non-uniformity is present, but inspection under a microscope indicated that the thickness variations are fairly small. The position of the absorber, shown in Fig. 1, is such that the height of the X-ray beam is around 5 mm, and the greater part of the foil is filled with radiation. Under these conditions a small microscopic non-uniformity does not affect the measurement, as the relative transmitted intensity I will be the same as for a uniform foil.

Let the mean thickness, as determined by weighing, be $\bar{x}$ and the thickness at a small area around a point $i = x_i$. What is measured in the spectrometer is the mean value

$$I = \overline{e^{-\mu x}} = \frac{1}{n} \sum_{i=1}^n e^{-\mu x_i}.$$

Put $x_i = \bar{x} + \Delta x_i$, where the thickness variation Δx_i is small. It follows that

$$\frac{1}{n} \sum_{i=1}^n e^{-\mu x_i} = \frac{1}{n} \sum_{i=1}^n e^{-\mu(\bar{x} + \Delta x_i)} = e^{-\mu \bar{x}} \cdot \frac{1}{n} \sum_{i=1}^n e^{-\mu \Delta x_i} = e^{-\mu \bar{x}} \cdot \frac{1}{n} \sum_{i=1}^n (1 - \mu \Delta x_i) = e^{-\mu \bar{x}},$$

if the area filled by radiation is so large that $\sum \Delta x_i = 0$.

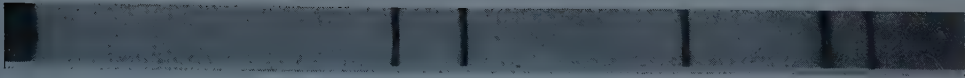


Fig. 10. The X-ray diffraction from the Ag-absorber recorded with Cu $K\alpha$ radiation. The reflexes from left to right are due to the following planes: 111, 200, 220, 311 and 222.

The result is then:

$$I = \overline{e^{-\mu x}} = e^{-\overline{\mu x}},$$

and the non-uniformity is of no consequence.

After evaporation and thickness determination the foil was mounted on an absorber frame as described in Section I: 4.

As already mentioned, great care was taken to avoid impurities in the absorber. As the recording of the Ag spectrum took a total time of more than one year, a check on the purity was necessary after the completed absorption measurements. This was done by X-ray diffraction. Fig. 10 shows the X-ray diffraction from the Ag absorber, and the only reflexes present are those from pure silver. It may also be mentioned that effects during the spectrum recordings indicating a progressive chemical change of the absorber material were entirely absent.

IV. Recording of spectra

1. Adjustments

Before the spectra are recorded the spectrometer has to be adjusted. The more permanent adjustments pertaining to the crystal and the slit are described in ref. [4] and Section I. The adjustments of the X-ray tube must be performed more often. They consist in setting the tube at the correct Bragg angle and in bringing the focal spot into the plane of the focussing circle. A description of these adjustments is found in ref. [5]. The Bragg angle of the tube must naturally be changed when the setting of the crystal is changed, but as the relation between distance intervals x on the precision screw and the changes in Bragg angle $\Delta\varphi$:

$$\Delta x = -R \cos \varphi \Delta \varphi \quad (\text{see Section I})$$

can be considered linear within the angular region of around 2° covered by an absorption edge measurement, this can be done without an experimental adjustment according to [5] for every wavelength. However, this latter adjustment is repeated whenever the spectrograph setting is changed with several degrees of arc.

Further, both tube adjustments are repeated when the X-ray tube cathode or target is changed as well as when the tube voltage and/or emission is altered. Finally, as the shape of the focal spot may change with increasing age of the coated cathode, a readjustment is performed whenever decreases in radiation intensity indicate this to be necessary.

A routine adjustment already mentioned in Section II: 3d is the setting of the channel of the discriminator.

In order to determine a suitable X-ray tube voltage, its influence on the intensity of the 2nd order radiation (at a fixed wavelength) was studied. The function obtained

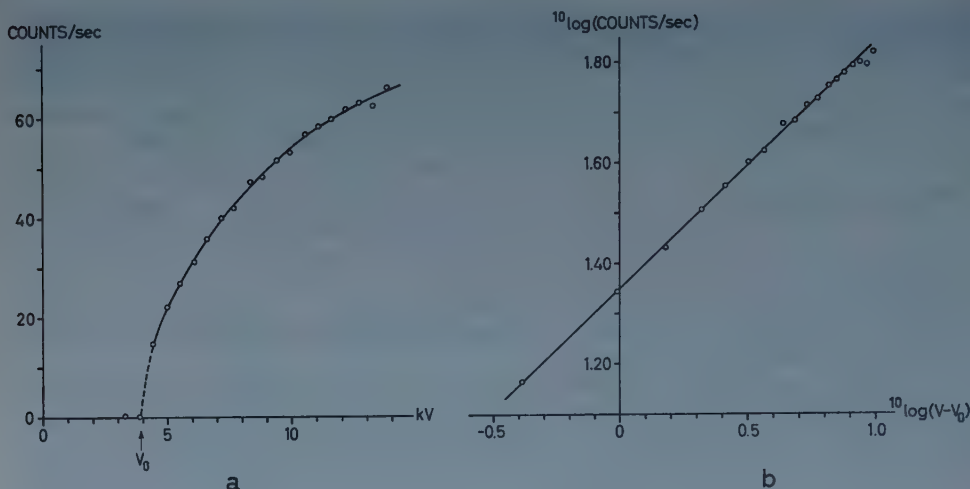


Fig. 11. The intensity of the 2nd order continuous radiation as a function of X-ray tube voltage at the wavelength $\lambda = 3130$ XU. V_0 is the excitation potential for this wavelength.

is represented in Fig. 11a. A log-log plot of this curve, Fig. 11b, reveals that the function is of the form

$$\text{Int}_\lambda = A (V - V_0)^{\frac{1}{2}},$$

where V_0 is the excitation potential for the wavelength λ and A a constant. It is apparent that little is gained by using voltages higher than, say, $4 V_0$. The relation between intensity and X-ray emission current is linear, however, and as a higher voltage makes an increase of the current possible it may for this reason be desirable to use high tensions. In the present case a voltage of 12.5 kV and an emission current of 40 mA was chosen.

2. Recordings

The mass absorption coefficients were calculated from

$$n - \nu = (n_0 - \nu_0) e^{-\mu_m d_m}, \quad (5)$$

where n and n_0 are the counting rates with and without Ag absorber respectively, ν and ν_0 the corresponding background counting rates and d_m the mass thickness of the absorber.

Even though n_0 proved to be fairly constant over the energy region of one edge recording, it was remeasured for each point on the curve. This procedure makes each absorption coefficient value more independent of the neighbouring ones. It also reduces the influence of a slow intensity time variation of n_0 and removes errors due to the presence of emission lines superimposed on the continuous spectrum. Finally, this method gives the true ratio of the intensities:

$$\frac{I}{I_0} = \frac{n \cdot h \nu}{n_0 \cdot h \nu} = \frac{n}{n_0}.$$

This is not the case if n_0 is measured at a different energy than n .

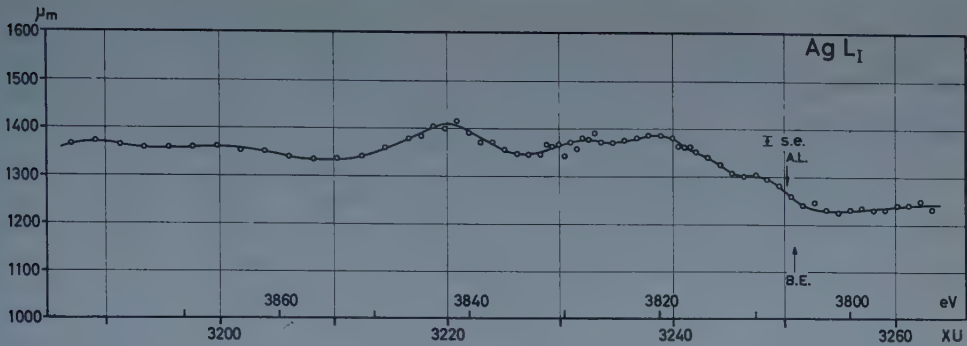


Fig. 12. The Ag L_I absorption spectrum. The mass absorption coefficient μ_m is given in $\text{cm}^2 \text{g}^{-1}$. s.e. indicates the standard error for each measured point. The position of the lowest inflexion point is indicated by an arrow marked A.L. (absorption limit). B.E. stands for the L_I binding energy as determined by Nordling *et al.* [26, 27].

The relation between the times spent on measuring n_0 and n influences the statistical accuracy of μ_m [14]. In the present case the optimum time distribution is $t/t_0 \approx 3.5$ for the high energy side of the absorption curve and $t/t_0 \approx 2$ for the low energy side. The actual counting times were $t = 1000$ sec, $t_0 = 300$ sec in the first case and $t = 600$ sec, $t_0 = 300$ sec in the second case, values close enough to the optimum ones.

A description of the method of determining ν_0 and ν is given in a previous paper [14]. As pointed out there, the determination need not be repeated for each single point. In fact it was only made when starting each of the edge recordings and repeated whenever the X-ray tube cathode or target was changed. As it was empirically found that the ratios $\kappa_0 = \nu_0/n_0$ and $\kappa = \nu/n_0$ were very nearly constant within the energy region covered by an absorption edge curve, the values of ν_0 and ν were taken as $n_0\kappa_0$ and $n_0\kappa$ for each individual measuring point. However, when n_0 increased owing to a superimposed emission line, the background values were taken from a point away from the line.

With the counting rates n_0 , n , ν_0 and ν measured, and d_m determined as described in Section III, eq. (5) gives the value of μ_m . The curves in Figs. 12–14 show the results of the recordings. Each point is the mean value of three absorption coefficient determinations obtained during three separate consecutive runs over the whole edge region. In this way the time interval between the repeated measurement of each point is rather great (of the order of several days), and the generally good agreement obtained between the three points indicates a high degree of reproducibility of the whole method.

In order to obtain an acceptable statistical accuracy the measuring time per point must be rather long and the total number of points for an edge recording restricted. It is thus of interest to estimate the longest wavelength distance between points that can be tolerated without the risk of overlooking details in the fine structure. In an absorption spectrum variations of $N(E)T(E)$, where $N(E)$ is the density of states and $T(E)$ the transition probabilities, are investigated with one of the L -levels as a probe, and the widths of these levels will set an ultimate limit to the resolution of the structure. To find this limit two identical Lorentz curves (representing one of the L -levels) with a distance A between the centres were added. It was found that

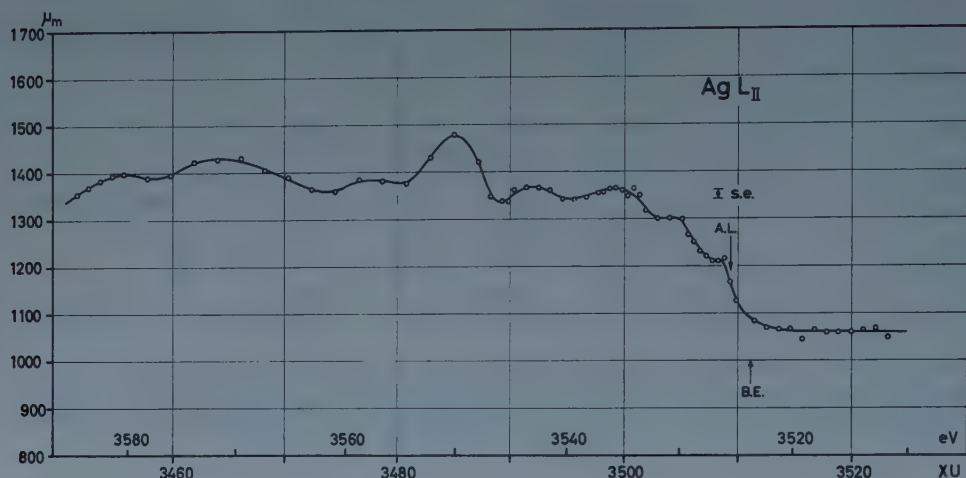


Fig. 13. The Ag L_{II} absorption spectrum. For explanations see text to Fig. 12.

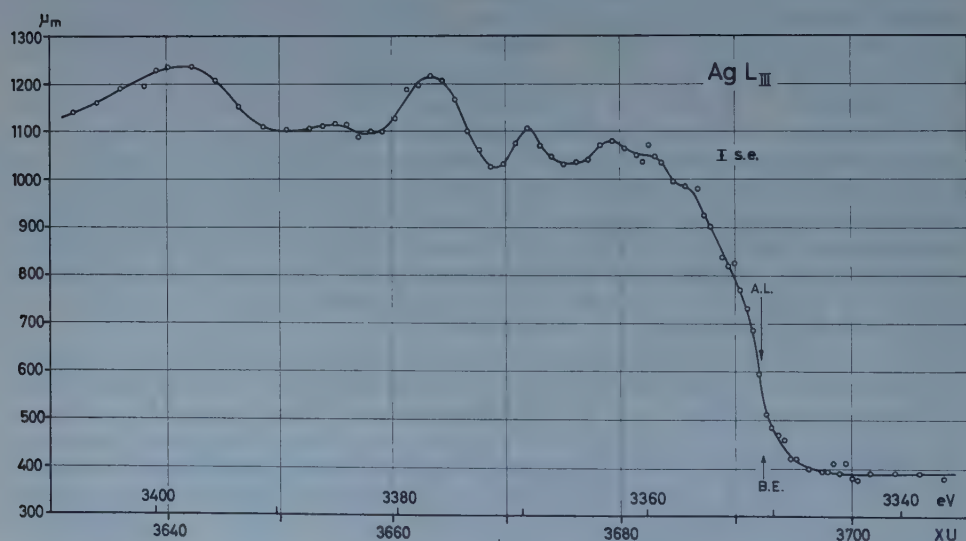


Fig. 14. The Ag L_{III} absorption spectrum. For explanations see text to Fig. 12.

the resulting curve was resolved into two separate peaks if $A > w/\sqrt{3}$, where w is the full half-width of the component curves. The width of the Ag L -levels are of the order of 2 eV [3], and $N(E)T(E)$ variation structures closer than around 1.3 eV cannot be resolved, however sharp they may be. This limit corresponds to circa 1.3 XU in the present region. Further, the spectral window has a width of around 0.5 XU (cf. Section VI), which further obliterates the structural details.

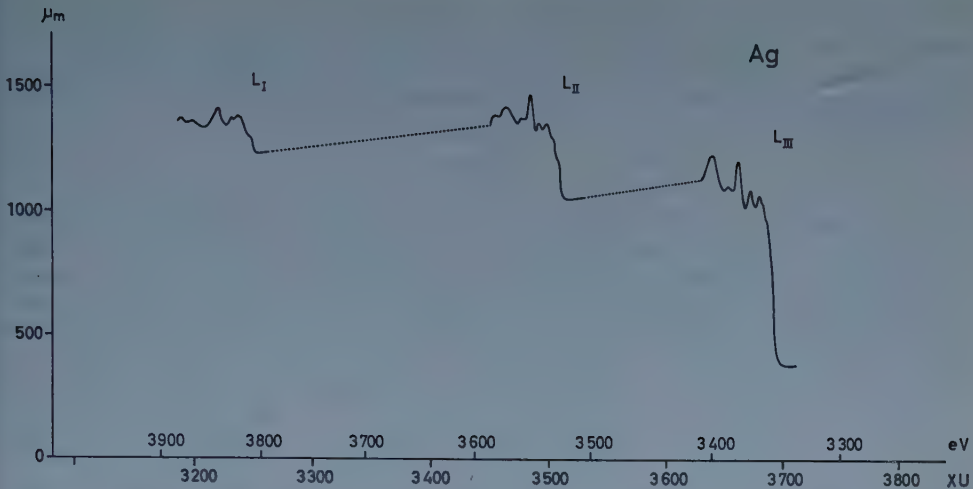


Fig. 15. The complete X-ray absorption spectrum of 47 Ag. The dotted lines represent regions where no measurements were made.

The result is that the points can be spaced at least 1 XU apart, and this has also been done. When a point indicated the possible presence of a structural detail the region was naturally investigated with points more closely spaced. This was also done for regions where especially high accuracy was desired, e.g. around the absorption limit itself. On the other hand, at relatively great distances from the edge, where no sharp structures are expected, intervals of up to 2 XU have been used.

The reference lines are: For L_{III} and L_{II} : Ag $L\beta_{2,15}$ and Ag $L\gamma_1$; for L_I : Sn $L\beta_1$ and Sn $L\beta_3$. All reference lines were recorded in the 2nd order. The wavelength values were those given in the Encyclopedia of Physics [7].

In Fig. 15 the whole L -absorption region is presented in one diagram showing the mutual positions and contrasts of the edges. The dotted lines indicate regions where no measurements were made.

V. Discussion of errors

The errors affecting the measurements can be divided into three groups, namely those influencing (a) the absolute values of the absorption coefficients, (b) the relative values, and (c) the wavelength measurements of structural details. However, as each particular error may naturally fall into more than one of these groups the disposition will here be somewhat different, one error at a time being discussed and the group it belongs to stated.

1. Statistical error

The "statistical error" in a limited sense here represents the error originating in the statistics of photon counting. This has been discussed in a previous paper [14], where eq. (14) gives a general expression for the relative standard deviation. It varies

with μ , since x and β in this equation are functions of μ , but in the present case the absolute value of the standard deviation will be nearly constant over the whole curves. It is found to be $17 \text{ cm}^2 \text{ g}^{-1}$ for each single μ_m measurement. As each point in the curves is the mean value of three determinations, the standard error due to counting statistics will be

$$\sigma_{\mu_m} = 10 \text{ cm}^2 \text{ g}^{-1}. \quad (6)$$

When deducing eq. (14) in ref. [14], it was assumed that the statistical error in the background counts ν_0 and ν was negligible. This still holds in the present investigation, partly because of the method used for determining ν_0 and ν , and partly because the background counting rates are only a few per cent of the total counting rates. A calculation shows that the contribution to the standard error is less than $0.5 \text{ cm}^2 \text{ g}^{-1}$.

However, owing to the method used for calculating the background at each separate point (see Section IV: 2), a proportional part (κ_0 and κ) of the statistical error in the counting rate n_0 is introduced into the value of the background counting rate. This increases the value (6) by around $1 \text{ cm}^2 \text{ g}^{-1}$, and the final standard error is given by

$$\sigma_{\mu_m} = 11 \text{ cm}^2 \text{ g}^{-1}. \quad (7)$$

This error, marked s.e., is indicated in Figs. 11–13. It belongs to all three groups (a)–(c) mentioned at the beginning of this chapter, though the influence on (c) is fairly small for regions with closely spaced points.

2. Error in absorber thickness

As mentioned in Section III the absorber thickness is measured by weighing. The total mass of the evaporated foil plus the substrate is determined with the aid of a sensitive balance. The areas (rectangles) of the substrate and the metal deposit are calculated, and the mass of the former, found from the known value of its mass thickness, is subtracted from the total mass. The mass thickness d_m of the absorption foil can then be found according to the equation

$$d_m = \frac{m_T - A_s d_s}{A_F}, \quad (8)$$

where m_T is the total mass of the evaporated foil plus substrate, A_s the area of the substrate, d_s its mass thickness, and A_F the area of the evaporated foil.

In the present case, where the determined mass thickness is 1.45 mg/cm^2 , the method gives a standard error

$$\sigma_{d_m} = 0.07 \text{ mg/cm}^2$$

or 5%. The influence of the error on the absorption coefficient values is also 5%, and it shifts the whole curve in the ordinate direction by this amount. It thus belongs mainly to group (a), as the ratio between any two ordinate values of the curve remains unaltered. Its influence on (c) is nil. As has been shown earlier no error due to microscopic non-uniformities of the foil is introduced as long as these are small, as there is reason to assume in the present case.

3. Scattering in the absorber

The absorption coefficients measured are the sum of the photo-absorption coefficient τ and the scattering coefficient σ . If one wants to interpret the result as meaning the former only, the influence of scattering must be corrected for. It is well known that for high atomic numbers and long wavelengths σ is small in comparison with τ , and this should apply in the present case, where $Z = 47$ and $\lambda \approx 3.5$ kXU.

The radiation is scattered both coherently and incoherently. At wavelengths far away from the absorption edges the intensity removed from the incident beam on account of coherent scattering can be calculated without difficulty. As the micro-crystals in the evaporated Ag foil have on the whole a random distribution, the latter can be assumed to act as a powdered crystal, and formulas for intensity calculations can be found in any standard text book on X-ray diffraction, e.g. ref. [18]. In the present case it is found that 4.4 % of the incident radiation is removed owing to coherent scattering. This corresponds to a scattering coefficient σ_{coh} :

$$\sigma_{\text{coh}} = 31 \text{ cm}^2 \text{ g}^{-1},$$

which is small though not negligible as compared with the total absorption coefficients.

However, close to the absorption edges anomalous scattering complicates matters. In general, the scattered intensity will decrease as a result of a decrease in the atomic scattering factor f_0 . In the case of K -edges the decrease can be fairly well computed theoretically, but for the L -edges no theory exists as yet. Experimentally it has been determined for tungsten L by Brentano & Baxter [19], who found a decrease in f_0 of around 10 close to the edges. The regions between the three L -edges were not investigated, however. If the value 10 is assumed also for silver, which seems permissible as the L -oscillator strength does not vary much with Z , and this value is further assumed to apply to the whole region L_I – L_{III} , which naturally is most uncertain, one finds as a rough approximation that 2 % of the incident radiation is removed owing to coherent scattering, corresponding to a scattering coefficient $(\sigma_{\text{coh}})_L$:

$$(\sigma_{\text{coh}})_L = 14 \text{ cm}^2 \text{ g}^{-1}.$$

The coherently scattered intensity from one atom can be written

$$I_{\text{coh}} = I_e \cdot f^2, \quad (9)$$

where I_e represents scattering by a free electron. Now it can be shown [20] that the intensity of the incoherently scattered radiation per atom may be represented by

$$I_{\text{incoh}} = R (Z - \sum f_n^2), \quad (10)$$

where $\sum f_n^2$ is the so-called electronic structure factor (tabulated in ref. [17]) and R the recoil factor. Approximately one finds that if all scattering directions are considered

$$\frac{I_{\text{incoh}}}{I_{\text{coh}}} \approx 0.01$$

in the present case and the influence of the incoherent scattering on the absorption coefficients can thus be entirely neglected.

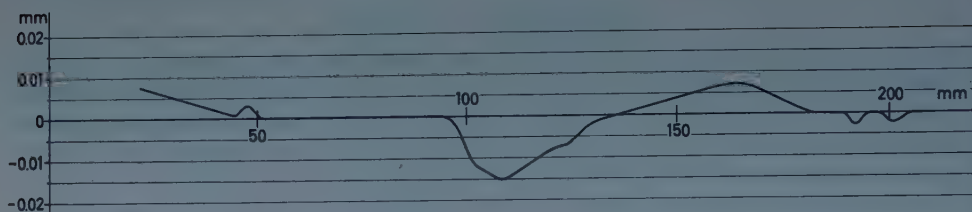


Fig. 16. The deviations from linearity of the precision screw. The abscissa is the distance along the screw and the ordinate the corrections (positive or negative) to be applied.

To sum up it may be said that the error made if the measured μ_m values are taken to represent τ_m alone is of the same magnitude as the statistical error. It works only in one direction, however, making the τ_m values somewhat too high. Further, as there is no reason to expect that σ has a detailed structure close to the edges, all variations in μ_m must be interpreted as variations of the photo absorption coefficient, and the error thus influences the absolute values only.

4. Errors in wavelength measurements

The wavelength of a structural detail in the absorption spectra is determined from the relation:

$$\lambda_x = \lambda_A + \frac{\lambda_A - \lambda_B}{x_A - x_B} (x_x - x_A), \quad (11)$$

where λ_x is the sought wavelength, λ_A and λ_B the wavelengths of the reference lines, x_A and x_B their positions on the precision screw and x_x the position of the structural detail.

All the quantities in the above expression have certain errors. Those of x_A , x_B and x_x are a combination of identification error and error due to the statistical fluctuation of the measured points. The former is small for the reference lines, which on the whole are sharp and symmetrical.

Apart from the errors contained in eq. (11) two more sources of error may influence the result, namely nonlinearity of the precision screw and temperature changes in the quartz crystal. The former was controlled by means of a high precision screw micrometer, and the result is found in Fig. 16, where the deviation from linearity is given as a function of the position on the screw. The greatest deviation is 0.022 mm (between the points $x = 108$ mm and $x = 164$ mm), which in the second order corresponds to 0.047 XU, which is less than the error in the wavelength determination of the reference lines (around 0.08 XU). The measured positions of the reference lines and the structural details of the absorption curves have all been corrected for the nonlinearity of the screw according to the curve in Fig. 16.

Errors are introduced by the temperature changes in the quartz crystal only if these occur during or between the recordings of the absorption spectrum and the reference lines. As an example it may be mentioned that a temperature change of 1° displaces a given wavelength by around 10^{-5} rad, corresponding to 0.04 XU in the 2nd order. The crystal temperature may change owing to heat from the X-ray target or a change in room temperature. The influence of the former was investigated

by making a series of recordings of a sharp emission line using widely different target temperatures. Though a systematic displacement of the peak position by less than 0.01 XU could have readily been detected by this method, the result was negative, indicating a sufficiently constant crystal temperature.

Changes in the temperature of the room can affect the crystal only very slowly because of the great mass of the spectrometer tank and of the fact that the spectrometer beam, on which the crystal holder is mounted, has thermal contact with the tank only at three rather sharp points, making the heat flow extremely slow. As the room temperature furthermore did not fluctuate much during the recordings, the thermal effects on the crystal appear to be negligible. This assumption is supported by the good reproducibility of the positions of the reference lines as obtained from recordings made at intervals of days and weeks.

All errors of significance are thus contained in eq. (11), and this can be used as the basis for the error calculation. The following expression is found for the variance:

$$\sigma_{\lambda_x}^2 = \left(\frac{x_x - x_A}{x_A - x_B} + 1 \right)^2 \cdot \Delta \lambda_A^2 + \left(\frac{x_x - x_A}{x_A - x_B} \right)^2 \cdot \Delta \lambda_B^2 + \left[\frac{(\lambda_A - \lambda_B)(x_B - x_x)}{(x_A - x_B)^2} \right]^2 \cdot \Delta x_A^2 + \left[\frac{(\lambda_A - \lambda_B)(x_x - x_A)}{(x_A - x_B)^2} \right]^2 \cdot \Delta x_B^2 + \left(\frac{\lambda_A - \lambda_B}{x_A - x_B} \right)^2 \cdot \Delta x_x^2. \quad (12)$$

Here the quantities $\Delta \lambda_A$ and $\Delta \lambda_B$ are the stated errors in the determination of the wavelengths of the reference lines. Δx_A , Δx_B and Δx_x , the errors in the positions on the screw of the reference lines and the absorption spectrum detail, are best estimated by studying the experimental points with their statistical errors and fitting a number of somewhat different curves to these.

The structural detail of the absorption spectrum that requires the highest precision in wavelength determination is the inflexion point of the lowest energy, which is taken to represent the "absorption limit", i.e. the transition to the Fermi level, and is thus of special interest. The reasons for this choice will be explained in Section VII. Here the wavelength error for this inflexion point will be given for each of the absorption curves separately.

Ag L_{III}. As previously mentioned, the reference lines were the *Ag L γ_1* and *Ag L $\beta_{2,15}$* lines, both recorded in the 2nd order. Their wavelength values were taken from the determination by Haglund [21], who estimates the errors

$$\Delta \lambda_A = \Delta \lambda_B = 0.08 \text{ XU}.$$

For the other quantities the following estimations are made:

$$\Delta x_A = \Delta x_B = 0.02 \text{ mm}, \quad \Delta x_x = 0.10 \text{ mm}.$$

This results in a standard error for the wavelength of the *L_{III}* edge

$$\sigma_{L_{III}} = 0.23 \text{ XU},$$

or in energy

$$\sigma_{L_{III}} = 0.21 \text{ eV}.$$

It is found that by far the greatest contribution to this error is Δx_x , while the influence of Δx_B and $\Delta \lambda_B$ is completely negligible.

Ag L_{II}. The same reference lines were used. Δx_x is here somewhat higher, namely 0.12 mm, as the edge is not as steep as that of *Ag L_{III}*. The result is

$$\sigma_{L_{II}} = 0.27 \text{ XU} \quad \text{or} \quad 0.27 \text{ eV.}$$

Here, too, Δx_x is the main source of error.

Ag L_I. The reference lines were Sn *Lβ₁* and Sn *Lβ₃*, recorded in the 2nd order. The wavelength values used are mean values of the determinations by Haglund (loc. cit.) and Wennerlöf [22]. The errors are estimated at $\Delta\lambda_A = \Delta\lambda_B = 0.08 \text{ XU}$. The estimations of the other errors are:

$$\Delta x_A = 0.01 \text{ mm}, \quad \Delta x_B = 0.02 \text{ mm}, \quad \Delta x_x = 0.15 \text{ mm}$$

(where *A* refers to β_1 and *B* to β_3). The relatively high value of Δx_x is explained by the low contrast in the edge. One finds

$$\sigma_{L_I} = 0.35 \text{ XU} \quad \text{or} \quad 0.41 \text{ eV.}$$

Again the dominating error is Δx_x , but $\Delta\lambda_A$, too, has a considerable influence owing to the fact that the distance between the edge and the closest reference line is here rather great.

5. Summary of errors

(a) *The absolute value of μ_m*

Here the statistical error and the error in the determination of the absorber thickness combine. The former is $11 \text{ cm}^2 \text{ g}^{-1}$ for all the curves and the latter 5 %, the result being for

L_{III}: H.E. $60 \text{ cm}^2 \text{ g}^{-1}$ (5 %); L.E. $23 \text{ cm}^2 \text{ g}^{-1}$ (6 %),

L_{II}: H.E. $70 \text{ cm}^2 \text{ g}^{-1}$ (5 %); L.E. $54 \text{ cm}^2 \text{ g}^{-1}$ (5 %),

L_I: The whole curve $70 \text{ cm}^2 \text{ g}^{-1}$ (5 %),

where H.E. and L.E. stand for the high energy side and the low energy side respectively.

However, if the curves are taken to represent the photo-absorption coefficient, all values are *too high* by an amount equal to the scattering coefficient for the absorber, which is estimated to be in the neighbourhood of $14 \text{ cm}^2 \text{ g}^{-1}$.

(b) *The relative value of μ_m*

Only the statistical error exerts an influence, and this is for all the curves $11 \text{ cm}^2 \text{ g}^{-1}$, which gives the following errors in per cent:

L_{III}: H.E. 1 %; L.E. 3 %,

L_{II}: H.E. 0.8 %; L.E. 1 %,

L_I: The whole curve 0.9 %.

It should be observed that this relative error in μ_m refers to each measured point in the diagrams. When a curve is fitted as well as possible to the points the relative errors of the values described by the curve will presumably be lower, as each point is then supported by the neighbouring ones. As a mathematical function describing the curve cannot confidently be assumed, no statistical treatment of this problem is possible, however.

(c) *The error in λ_e and E_e*

λ_e and E_e , the wavelength and energy of the absorption limit (i.e. the lowest inflexion point) have the errors

$$\begin{aligned} L_{\text{III}}: & 0.23 \text{ XU or } 0.21 \text{ eV;} \\ L_{\text{II}}: & 0.27 \text{ XU or } 0.27 \text{ eV;} \\ L_{\text{I}}: & 0.35 \text{ XU or } 0.41 \text{ eV.} \end{aligned}$$

VI. The resolving power of the spectrometer

The fact that the spectrometer has a resolving power that is not infinite distorts the measured absorption spectra and thus acts as a special type of error. An investigation by Parratt [17] shows this effect very clearly.

If the relative transmitted intensity is $I(\lambda)$ at infinite resolving power, the experimentally obtained function for the relative transmitted intensity $E(\lambda_0)$ is related to this by the folding integral

$$E(\lambda_0) = k \int_{-\infty}^{+\infty} I(\lambda) \cdot P(\lambda - \lambda_0) d\lambda, \quad (13)$$

where $P(\lambda - \lambda_0)$ is the spectral window function (λ_0 being the wavelength for which the spectrometer is set) and k a normalization constant. However, even if the exact window function were known it would in principle be impossible fully to correct the experimental values for the spectral window, as the function $I(\lambda)$ is not uniquely defined by eq. (13). True structural details obliterated by the folding with the window can never be recovered by some mathematical process, as they are no longer contained in the information supplied by the spectrometer. In many cases one can all the same make a good guess at the shape of the true curve, especially if the distorting influence of the window is small and if a lower limit can be set to the widths of the structures in the true curve. As has been shown in Section IV: 2, this is possible in the present case owing to the widths of the L -levels.

The great disadvantage of a bent crystal spectrometer as compared to the two-crystal type is the difficulty in obtaining reliable information about the spectral window. An interesting method would be to record a γ -line. The profile curve would then represent the spectral window, as the width of the line itself is negligible. With the present spectrometer this method is not possible, as the energies of sufficiently intense γ -lines are too high.

Instead comparisons of line widths have been made. Parratt [3] has measured the width of the Ag $L\alpha_1$ line, using a two-crystal spectrometer and correcting for instrumental broadening. He found

$$w_L = 3.26 \text{ XU},$$

where w_L is the full width at half maximum. The experimental, uncorrected width obtained with the present spectrograph is [5]:

$$w_T = 3.45 \text{ XU}.$$

Now the width w_L of a line combines with the width w_S of the spectral window to give a total width w_T according to

$$w_T^n = w_L^n + w_S^n. \quad (14)$$

The value of the exponent has been discussed in several papers (see ref. [5] and references therein), and values ranging between $n = 1$ and $n = 2$ have been proposed. The best value of n for the present spectrometer is difficult to estimate, but a discussion based on the line widths just mentioned may clarify matters.

We know that the shape of an X-ray emission line is very closely Lorentzian for transitions between two inner levels, as is the case with Ag $L\alpha_1$ ($L_{III} M_V$). Let us for the spectral window assume three different shapes: (1) rectangular (R), (2) Gaussian (G), (3) Lorentzian (L). The real window is most certainly of a more complicated shape than any of these, but they may serve as extreme models. A folding of the window with the Lorentzian line then gives the following exponents in eq. (14):

- (1) $L + R$; $n = 2$,
- (2) $L + G$; $n = 1.4$,
- (3) $L + L$; $n = 1$.

The value of n in case (2) varies somewhat with the relation between the widths of the Lorentzian and Gaussian, and the value stated applied to the present case. The consequence is that the smaller the tails of the spectral window, the higher is the value of n . For these three n -values, the half-width w_s of the window according to eq. (14) turns out to be:

- (1) Rectangular window: $w_s = 1.73 \text{ XU}$,
- (2) Gaussian window: $w_s = 0.56 \text{ XU}$,
- (3) Lorentzian window: $w_s = 0.19 \text{ XU}$.

In order to study the influence of the slit-width on the resolving power it is convenient to regard the spectral window as a combination of the rectangular window of the slit and the rest of the window, here termed crystal window, as it is mainly created by the diffraction pattern of the crystal plus a number of focussing defects. The width of the slit window w_D combines with that of the crystal window w_C according to

$$w_s^n = w_C^n + w_D^n. \quad (15)$$

For the total window the shapes R , G and L have previously been assumed. However, as a folding with a rectangle having a relatively narrow width does not essentially change the shapes of these curves, the same assumptions can be made concerning the crystal window. For the values of the exponent in eq. (15) the following values are then found:

- (1) $R + R$; $n = \infty$,
- (2) $R + G$; $n \approx 2.6$,
- (3) $R + L$; $n = 2$.

Case (1) is valid only if the rectangles have different widths.

Again the value of n in case (2) varies with the ratio between the two widths, and the one chosen here applies to the present case. During the recording of the Ag $L\alpha_1$ line (2nd order) the slit-width was 0.085 mm, which, according to eq. (3), corresponds to a wavelength region $\Delta\lambda = 0.11 \text{ XU}$ in the 2nd order. Reducing the previously obtained w_s values for the slit-width one obtains:

- (1) Rectangular window: $w_C = 1.73 \text{ XU}$,
- (2) Gaussian window: $w_C = 0.56 \text{ XU}$,
- (3) Lorentzian window: $w_C = 0.155 \text{ XU}$.

The influence of the slit-width mentioned above is thus negligible in cases (1) and (2).

Adell *et al.* [23] have studied the widths of rocking curves of quartz 10 $\bar{1}$ 0, and extrapolation of their results to the Bragg angles used here gives a half-width of the rocking curve $w = 0.34$ XU. The rocking curve is essentially a combination of the diffraction patterns of the two crystals. Again it is unknown how they combine, but the half-width for a single crystal is probably somewhere around 0.20 XU. This value, which is for a perfect, unstressed crystal, is definitely a lower limit for the present width of the crystal window, and this must consequently have *lower* tails than a Lorentzian. On the other hand, the tails are present to quite a large extent, as Parratt [17] has showed in the case of unstressed crystals. It thus seems reasonable to assume a spectral window model somewhere between the Lorentzian and Gaussian and perhaps closer to the latter.

For the recordings of L -absorption spectra the slit-width was for intensity reasons increased to 0.15 mm, corresponding to a wavelength region of 0.19 XU. For the same three models the total window widths w_s then are:

- (1) Rectangular window: $w_s = 1.73$ XU,
- (2) Gaussian window: $w_s = 0.57$ XU,
- (3) Lorentzian window: $w_s = 0.25$ XU.

Although the slit-width is fairly large, its influence is again negligible in cases (1) and (2).

In order to get a rough estimate of the distortion of the absorption spectra caused by the spectral window, the experimental Ag L_{III} curve (Fig. 14) was transformed into a relative-intensity curve and taken to represent the true function $I(\lambda)$ in eq. (13). It was then folded with the three model windows R , G , and L having the widths stated above. The intention was to arrive at a corrected intensity function through an iteration process. However, it turned out that the three new curves when transformed back into absorption coefficient functions were extremely close to the original one. The greatest deviations, around 1 %, were found for the Lorentzian window, but as has been shown earlier this model is impossible in the present case. The other two curves gave maximum deviations of less than 0.3 %. The conclusion is that the spectral window has a totally negligible effect on the present absorption coefficient measurement.

Finally, it must be emphasized that the widths of the L -levels are of great importance if one wishes to interpret the L -absorption spectra as a picture of the product $N(E)T(E)$, where $N(E)$ is the density of states and $T(E)$ the transition probability. According to Parratt [3] the L -level widths are:

$$L_I: 5.3 \text{ eV}, \quad L_{II}: 2.2 \text{ eV}, \quad L_{III}: 2.0 \text{ eV}.$$

Moreover, as the levels are Lorentzian in shape, it is apparent that the finer details in the $N(E)T(E)$ function are probably smoothed out to a great extent. It may here be mentioned that the disturbances in this function due to heat motion are of the order of kT , which at room temperature equals only 0.03 eV. As the term "absorption spectrum" must be applied to the function uncorrected for the width of the inner level, no effort has been made here to make such a correction.

VII. Results and discussion

As mentioned earlier the inflexion point having the lowest energy is—somewhat arbitrarily—taken to represent the absorption limit. In almost all previous works on X-ray absorption this has also been done, and tables of electron energy levels have been calculated from the values thus obtained. The reasons for choosing this special point are not wholly conclusive, but on the other hand the choice of any other point is even less motivated.

In the ideal case of constant density of empty levels in the conduction band and constant transition probability Richtmyer, Barnes & Ramberg [24] showed that the inflexion point is indeed the correct choice. The experimental work of Soules & Shaw [25] on the *K*-absorption spectrum of gaseous and solid argon, where the peak of the first sharp absorption line in the gas coincides with the inflexion point of the edge in the solid, indicates the same. Further it has repeatedly been shown that in metals the inflexion point of the absorption edge and that of the high-energy edge of the corresponding emission band frequently nearly coincide.

Naturally matters are complicated by transition probabilities, overlapping energy bands and excitation states due to the ejected photo-electron. It is hoped that the results of the present research project covering the *L*-absorption spectra of 47 Ag–52 Te may clarify matters. The intention is to compare the X-ray values of the electron energy levels, assuming these to correspond to the lowest inflexion point of the absorption spectra, with the values obtained by Nordling, Bergvall & Hörnfeldt [26, 27] from energy measurements of the ejected photo-electrons. Their values, indicated B.E. (binding energy) in Figs. 12–14 and Table 2, have a high degree of precision, and the method by which they are obtained is free from the interpretation difficulties present in X-ray measurements.

Table 1 gives the wavelengths of the absorption limits. Around the inflexion point corresponding to this limit the absorption curve can be considered linear, and the inflexion point is chosen at the middle of this linear part. The reasons for the great discrepancies between the present and earlier values are mentioned in the introduction to this paper.

Table 1. The wavelength in XU of the *L*-absorption limits of 47 Ag. The wavelength of L_{III} that can be read from Parratt's [3] diagram, mentioned in the introduction, is $\lambda = 3694$ XU.

Edge	Present	Coster & Mulder [1]	Van Dyke & Lindsay [2]
L_I	3249.8 ± 0.4	3244.8	3247.4
L_{II}	3509.3 ± 0.3	3506.2	3506.7
L_{III}	3692.1 ± 0.2	3693.0	3690.8

In Table 2 the energy values are given. These are computed according to

$$E = \frac{12372.2 \times 10^3}{\lambda},$$

where λ is in XU and E in eV. The constant used is due to Du Mond & Cohen [28] and is the same as that used by Nordling & Bergvall in the B.E. calculations.

Table 2. The energies in eV of the L -absorption limits of 47 Ag. "B.E." refers to photo-electron measurements. The errors are standard errors.

Edge	Present	B.E. [26, 27]
L_I	3807.0 ± 0.4	3806.2 ± 0.3
L_{II}	3525.5 ± 0.3	3523.7 ± 0.3
L_{III}	3351.0 ± 0.2	3350.8 ± 0.3

Here it will only be stated that the L_I and L_{III} values coincide with the B.E. values within the limits of errors, while the L_{II} value disagrees. A detailed discussion of these facts will appear in a later paper, when the work on 48 Cd-52 Te now in progress is completed.

Finally, some attention must be paid to the extended fine structure on the high-energy side of the edges, the so-called Kronig structure. Attempts to identify the absorption minima with those stated in Kronig's theory [29] were unsuccessful. This is, however, not surprising, as the theory is based on idealized conditions (completely free electrons) and does not take into account such facts as multiplicity factors of the reflecting planes or varying atomic scattering coefficients for the electron waves. Possibly the new theory based on quasi-stationary states developed by Hayasi [30] will give better results. This theory is as yet confined to K -absorption edges, however.

A comparison with the fine structure for L_{III} obtained by Parratt [3] reveals a close resemblance, the difference being mainly that his spectrum shows a number of very small structural details not found in the present curve. Whether these small details are real is difficult to say as Parratt has not stated the accuracy with which his experimental points are measured.

As seen in Figs. 13 and 14 the Kronig structures in L_{II} and L_{III} are very similar to each other. This appears more clearly in Fig. 17, where the positions of the absorption maxima (short lines) and minima (long lines) are indicated, the absorption limits being taken as zero energy. In L_{II} , however, the positions are systematically somewhat displaced in relation to those of L_{III} . This displacement is around 1.7 eV or the same as the discrepancy between the X-ray and B.E. values for the L_{II} energy (see Table 2). This is probably a significant fact, indicating that there may be a lower unresolved inflexion point in L_{II} than the one chosen from the present curve. This will be further discussed in a later paper, when more experimental data are at

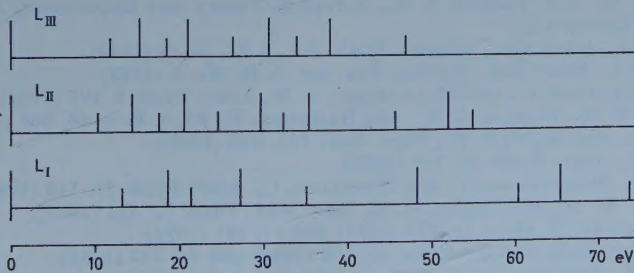


Fig. 17. The positions of absorption maxima (short lines) and minima (long lines) in the extended fine structure of the three L -absorption spectra. The lowest inflexion point is taken as zero level in each case.

hand. The positions of maxima and minima in L_I cannot be correlated with those in L_{II} and L_{III} . This fact has previously been observed for several elements (see e.g. ref. [31] and [32]), and is to be expected as the electron is not completely free as close as 50–60 eV from the edge and thus the transition probability is different for the s - and p -states. The great width of the L_I level (5.3 eV according to Parratt [3]) and the low contrasts in the structure further make the measurements of the positions rather uncertain.

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